Mapping hole mobility in PTB7 films at nanoscale

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Abstract. The nanoscale hole mobility in organic semiconducting polymer PTB7 is quantified by using conductive-AFM (C-AFM) measurements in space charge limited (SCLC) regime. The obtained current map of the neat PTB7 film is explained in terms of non-uniform built-in voltage and variations of hole mobility. For mobility estimation, the semi-empirical model of SCLC, known from previous works, was modified and applied. It is found that the values of built-in voltage in C-AFM measurements are usually several times larger than ones derived from macroscopic measurements. It is also shown that value of hole mobility in PTB7 film depends on location and varies in more than two times. These mobility variations are connected with nanoscale film structure revealed by other methods.

1. Introduction

One of the most important achievements of the recent progress in synthesis of new materials for organic photovoltaics (OPV) was introduction of the new thiophene based donor with abbreviation PTB7 (Poly [[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl][3-fluoro-2-[(2 ethylhexyl) carbonyl]thieno[3,4-b]thiophenediyl]]) [1]. The improved processing conditions and device architecture allowed achieving 9.2% [2] and later 10.02% [3] power conversion efficiencies on solar cells with PTB7:PC71BM active layer. Thus, blend PTB7:PC71BM was under intensive investigation since its first introduction and structure and properties of this compound were extensively examined by different methods [4-8]. One of important parameters of organic semiconductors, which influences performance of polymer:fullerene solar cells, is a charge carrier mobility. Mobility can be determined by different methods, in particular, by measurements of the space charge limited current (SCLC) [2, 9-12]. Influence of polymer hole mobility on performance of PTB7:PC71BM solar cell was discussed earlier [10,12]. Beside structure of bulk heterojunction, characterization of the electrical properties of organic semiconductors at nanoscale is one of the important directions towards understanding the physics of organic electronic devices and improving their performance. The use of small electrodes to form local contacts is required for such nanoscale measurements. Thus, Atomic Force Microscopy (AFM) equipped with conductive probe (conductive-AFM or C-AFM) is a promising tool for probing local electrical properties of materials. The quantitative analysis of local current-voltage (I-V) curves obtained by C-AFM is an attractive method of characterization of the local electrical properties, such as charge carrier mobility, quantum efficiency, local open circuit voltage, and short circuit current [8, 13-16].

However, complicated geometry of the electrodes in C-AFM makes any quantitative analysis much more challenging than just use of standard Mott-Gurney law [10], which is suitable for flat electrodes. The semi-empirical model for local mobility measurements by C-AFM was introduced by O. Reid et al. [16] and it was applied to standard OPV materials such as P3HT and MDMO-PPV.

Here, we use C-AFM for analysis of the local conductivity in PTB7-based films and apply modified semi-empirical model for calculation of the nanoscale mobility and its variations caused by film structure.

2. Experimental

PTB7 films were produced by spin-coating from solution in chlorobenzene on glass/ITO/PEDOT:PSS as described elsewhere [7,8]. Different spin-coating rates were used in order to obtain a set of PTB7 films with different thicknesses ranging from 50 to 120 nm. The C-AFM measurements were performed by AFM Smart1000 (AIST-NT) in contact regime. The gold-coated probes CSG10/Au were utilized for C-AFM. The alternating mode of current measurements implemented in software was employed, which implied the lift of the probe from surface when movement from point to point was executed in order to reduce the sample damage. Tip-sample force was estimated from force-distance measurements for each experiment being in the range of 5-10 nN. Cantilever force constant was determined by Sader method implemented into AFM software. Tip-sample area was estimated corresponding to Hertzian contact theory with modulus elasticity of PTB7 taken from recently published data [17]. Gold coated tip radius estimated using SEM was 45 nm. The wavelength of AFM laser was 1300 nm, being far from light adsorption maxima of the films [2,7]. All samples were kept inside nitrogen filled glove-box and taken out just before AFM measurements. Conventional SCLC measurements were performed on devices with structure glass/ITO/PEDOT:PSS/PTB7 film/Au-electrode using potentiostat Autolab PGSTAT302N. The hole mobility calculations were performed corresponding to the unified protocol published recently [11]. Software Nova (NT-MDT) was utilized for drawing local mobility and built-in voltage maps.

3. Results and discussions

Nanoscale topography of the neat PTB7 film shown in Figure 1a is very flat and shows very small height variations of less than 10 nm in amplitude. These variations are much smaller than film thickness L=102 nm, determined by AFM measurements of the scratch. The current distribution map obtained by C-AFM has nearly no correlation with topography image (Fig. 1). The contrast in current image reveals grain and fiber-like structures, while topography image is rather flat. Current variations in one scan are significant and difference between current level is up to several times in different locations. Thus, even neat PTB7 film demonstrates highly non-uniform electrical properties at nanoscale. In order to understand mechanism of local conductivity, measurements of I-V curves were performed by C-AFM on film surface at the grid of 5x5 points. Figure 2a shows cross-section of obtained data at tip voltage U_t=+5V on 0.5x0.5 μm^2 area, and Figure 2b demonstrates all 25 I-V curves. It is clearly seen that all the curves are different and, thus, different local electrical characteristics are expected. The average I-V curve plotted in double logarithmic scale represents a straight line with a slope 3.2, which is reduced to

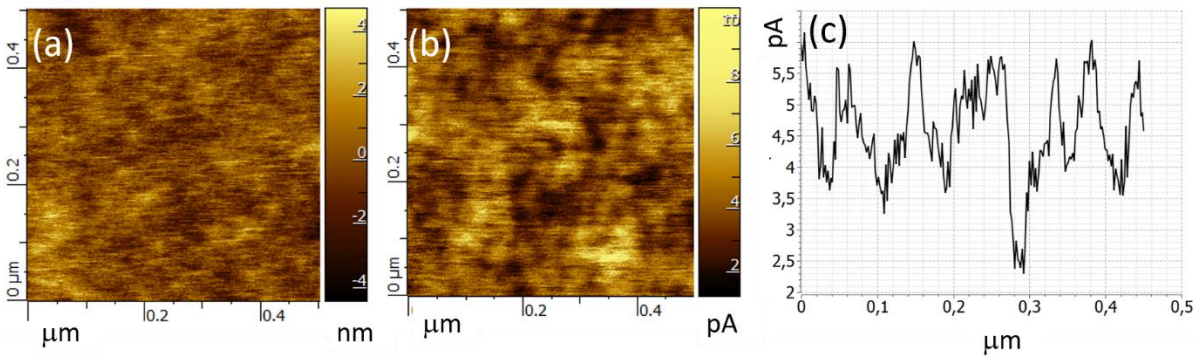

Figure 1. C-AFM results: (a) topography, (b) current, (c) cross-section of (b).

2.0 after taking into account built-in voltage U_{bi} [18], clearly indicating that space charge limited current takes place (Fig. 2c). Corresponding to energy levels of PTB7 and electrodes used, the C-AFM contrast is caused by hole current through Au probe/PTB7/PEDOT:PSS/ITO [7-8]. Only positive voltages on the tip are used for analysis, which correspond to hole injection from tip to polymer. Then obtained results can be used for calculations of hole local mobility in PTB7 film. For this purpose, the protocol of mobility calculation [11], as well as semi-empirical model of SCLC adapted for C-AFM measurements [16], were utilized by us for hole mobility estimation.

First of all, series of PTB7 films with different thicknesses were measured in the same manner by C-AFM and average I-V curve was used for current density J vs. film thickness L plot. From these data the dependence $J \sim L^{-1.7}$ was derived, which lead to modified equation for local mobility [16]:

$$I = A_{eff}\ \alpha\ \varepsilon_0\ \varepsilon\ \mu\ e^{0.89\gamma\left(\frac{U}{L}\right)^{\frac{1}{2}}}\ \frac{U^2}{L^3}\ \delta\ \left(\frac{L}{d}\right)^{1.3}, \qquad (1)$$

where α=8.2 is a parameter from numerical calculations [16], ε=3.5 is material permittivity, μ is the hole mobility at zero field, γ is field dependence parameter of the mobility, L is the sample thickness, d is the tip-sample contact diameter, δ=7.8 is the scaling factor for fitting C-AFM mobility to macroscopic data [16].

Corresponding to our macroscopic SCLC measurements on the same structure, parameter γ is equal to zero and we will use it in nanoscale calculations. The voltage U in (1) must take into account the value of built-in voltage U_{bi} [18]: $U=U_t-U_{bi}$. The value of U_{bi} was estimated as 0.25 V for macroscopic data. However, for C-AFM data the same method of estimation applied to local *I-V* curves gives significantly higher values of U_{bi} between 1.2 and 1.8 V with rms value 0.18 V. Such difference between macroscopic and C-AFM results is not clear and can be explained by influence of surface properties, e.g., water or double layers at interfaces as well as some changes of surface properties under the probe when AFM contact mode is used. No correlation between tip-sample force and U_{bi} was found. Mapping of U_{bi} on surface is shown in Figure 3a. Variations of U_{bi} on the surface can be caused by local surface properties as well as non-uniform structure of PEDOT:PSS layer.

Taking into account $U_{bi}(x,y)$ and using Eq. (1), distribution of hole mobility on the $\mu(x,y)$ surface can be obtained. The results of mobility mapping are shown in Figure 3b. Each pixel in Figures 2a and 3 corresponds to the area 100x100 nm^2, being roughly a size of current cross-section at PEDOT:PSS as estimated by modelling [16]. One can see that there is no direct correlation between current, U_{bi}, and mobility distributions, i.e. despite proportionality between current and mobility in Eq. (1), the influence of non-uniform $U_{bi}(x,y)$ on current distribution is essential. The performed calculations were made manually with limited image resolution. Increased number of measured I-V curves will lead to image similar to Figure 1b; however, it requires automated procedure due to a large data array. The average value of nanoscale mobility is 1.17*10^{-8} m^2/(Vs), which is close to macroscopic value of 1.34*10^{-8} m^2/(Vs) obtained by regular SCLC on the same structure. At the same time, variations of mobility in more than 2 times from 0.69 to 1.59 10^{-8} m^2/(Vs) may be explained by non-uniform structure of PTB7 films, which was revealed earlier by XRD [4,5]. The rms value of the hole mobility is 0.22*10^{-8} m^2/(Vs), which is almost 20% from the average mobility.

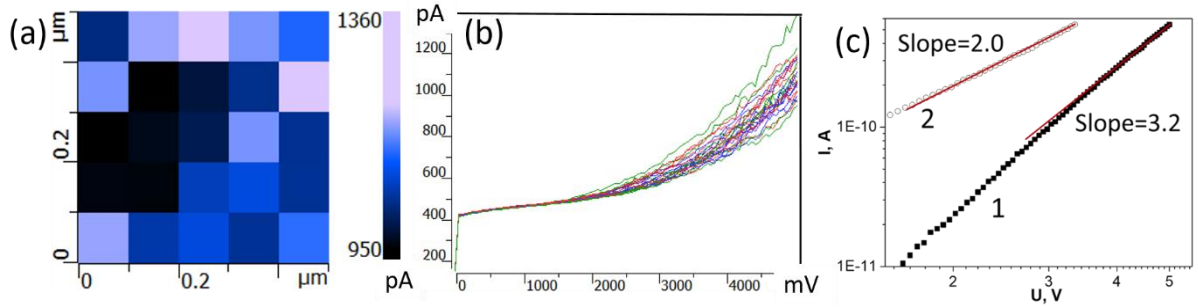

Figure 2. (a) Section of array of 25 I-V curves at U=+5V; (b) 25 I-V curves; (c) average I-V curve in double logarithmic coordinates: 1- initial voltage scale, 2 – U_{bi} is taken into account.

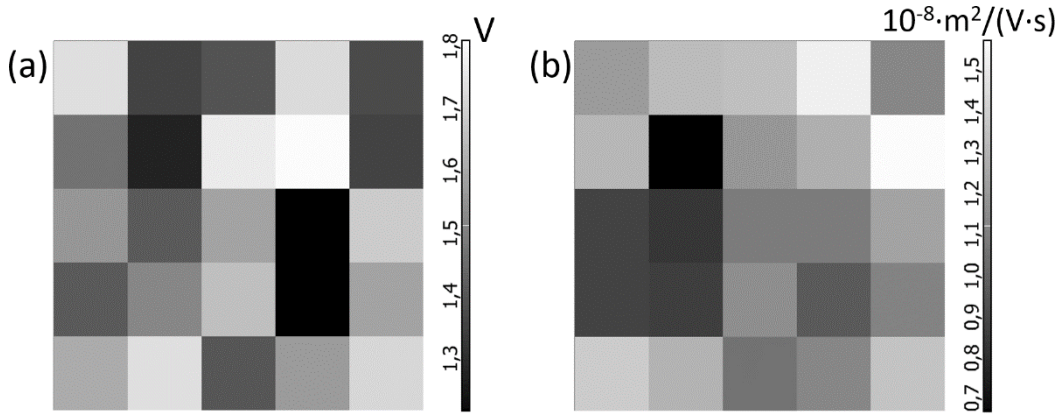

Figure 3. Distribution of (a) U_{bi} and (b) hole mobility μ for the same area as shown in Figure 2a.

Corresponding to XRD results, the PTB7 spin-coated films consist of nanocrystalline areas inside amorphous matrix [4,5]. Since current area between sharp golden tip and flat opposite electrode has gradually increased cross-section, the top layer of film has larger influence on detected current. In top layer of the film, size of ordered areas of PTB7 is closer to current cross-section and then structure influences current, producing contrast in C-AFM image. Thus, contrast in Figure 1b and Figure 2a reflects mainly structure in top layer of PTB7 film. This current contrast at high voltages (U-U_{bi}>1 V) can be described in terms of non-uniform built-in voltage and hole mobility. The hole mobility variations may also be explained by different amount of crystalline and amorphous polymer inside volume, where charge carrier flow occurs.

4. Conclusion

The variations of local current in PTB7 film may be explained by influence of nanoscale structure in top layer of the film. The current image can be decomposed into two images with distributions of local built-in voltage and hole mobility by using semi-empirical equation, which describes local I-V dependences in SCLC regime. Local mobility values on surface of film caused by local structure differ in more than two times and have rms value $0.22*10^{-8}$ $m^2/(Vs)$, which is almost 20% from average mobility.

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